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Low temperature CL investigation of BN1 vibronic structure in c-BN

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Abstract

A full vibronic spectrum has been measured for the first time by LNT Cathodoluminescence in HPHT c-BN amber-coloured microcrystalline samples. The related BN1 centre at 3.293 eV seems not created by electron irradiation in this case and the accurately determined phonon energy (141 ± 3 meV) could be related to LO phonon at *X* point in Brillouin Zone (BZ) of c-BN, as determined by CL results obtained at indirect gap. Consequently, BN1 centre has not the full cubic symmetry of c-BN, as being due to N interstitials. The interpretation of the results is possibly two-fold: either we are observing a vibronic spectrum with ZPL at BN1 centre, together with other two centres called PF-1 and PF-2 at 3.573 and at 3.412 eV, respectively, or, since all the 6 or 7 observed peaks are exactly equally spaced, the whole vibronic spectrum is related to a ZPL line at 3.573 eV. This new interpretation seems to be in better agreement with the general theory of colour centres.

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1. Introduction

Cubic boron nitride (c-BN) is a wide band gap semiconductor still in an early stage of development with respect to diamond, but with the advantage of being the stable phase at room temperature and of being easily doped both p and n type, a fact that opens the way to several kinds of possible devices. More than 25 different centres have been discovered until now not only in HPHT (High Pressure High Temperature), but also in CVD deposited c-BN: many of them are created by irradiation and their importance is based both on the possibility of future production of ion implanted devices and also on the likely use of c-BN devices in a radiation hard environment.

The major difference with respect to diamond is related to the existence of off-stoichiometry and to the binary nature of c-BN, with the consequence of a larger variety of native defects, and to the polar nature of the B–N bond (25% ionic in character), which gives rise to polar longitudinal optical phonons (LO) strongly interacting with incident or emitted light. The investigations on these centers are carried out by Photoluminescence (PL), by Cathodoluminescence (CL) and by Ionoluminescence (IL or IBIL, Ion Beam Induced Luminescence) [1–5]. Also Raman

spectrum of c-BN has been extensively investigated [6–9]. Centres have been reported from 1.55 up to 4.05 eV, being generally the radiation-induced centres such as RC1, RC2, RC3, etc., much more intense than “natural” centres such as PF1 and PF2, for instance [1]. One of the more recently reported centre, indicated as BN1, was found in electron irradiated samples (230–300 keV, about 10^{20} e/cm²), with a ZPL (Zero Phonon Line) placed at 376.4 nm (3.293 eV) and with some phonon (LO, TO) replicas at the anti-Stokes side [1]. Because of its similarity with the 3.188 eV centre in electron irradiated diamond, attributed to interstitial nitrogen, and also because calculations [8,9] indicate a lower formation energy for N_i with respect to B_i, it was concluded that this centre was created only during electron irradiation. Raman spectra quote very consistently a LO phonon line at 1305 cm^{−1} (161.5 meV) and a TO line at 1054.7 cm^{−1} (130.5 meV) [7] and these values are in close agreement with phonon replicas reported previously at 7 K under 325 nm excitation, from which a LO energy between 159.7 and 163 meV can be evaluated from the quoted PL spectrum. The authors report that below 200 keV only very weak BN1 luminescence was observed under UV illumination, which completely disappeared after irradiation at 150 keV. CL seems to be a more powerful method with respect to excitation mode, which does not follow specific selection rules and can fill up any radiative recombination centre. In fact [10] by CL some phonon-assisted free-exciton luminescence lines were

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discovered quite recently at 83 K below the indirect band gap of c-BN (6.25 eV) and were attributed to LO_x , LA_x , TO_x and TA_x phonons with energies of 138, 124, 104 and 88 meV, respectively, at X point in BZ instead of Γ point, to which first order Raman measurements refer.

2. Experimental

Two free-standing c-BN samples, CBN6 and CBN7, in the form of sintered microcrystalline powders in platelets of comparable dimensions (1.2 mm thick, 8.4 mm in radius), were investigated. The grains had typical dimensions of some tens of microns (10–40). The powders were produced by HPHT method by using $\text{Ca}_3\text{N}_2 + \text{LiF}$ as precursors and were amber coloured.

Secondary electron (SE) and BSE (BackScattered Electrons) images were obtained by means of a Cambridge S360 Scanning Electron Microscope which, for CL measurements, was equipped with an Oxford Mono-CL2 apparatus together with a MMR Technologies cold stage as a sample holder.

Together with CL and SEM maps, some other maps were obtained by recording directly EDS X-ray characteristic spectra in an energy region between Be and Si, in order to avoid in any case to include materials different from c-BN. In CL measurements, probe current was typically 5 nA over an investigated area of $5 \times 5 \mu\text{m}$; the temperature was varied between 86 and 300 K.

3. Results and discussion

Fig. 1 is a topographic secondary electrons SEM image of the sample CBN7 under study which has been mixed with an EDS map in which the different characteristic X-rays are selected in energy between 0.1 keV (deep red) and 1.9 keV (deep blue). The selected regions for CL measurements, labelled as D, E and F for this sample, are in the centre of the grains and do not include regions of different colour, which can include different elements. CL spectra as obtained at 297 K on

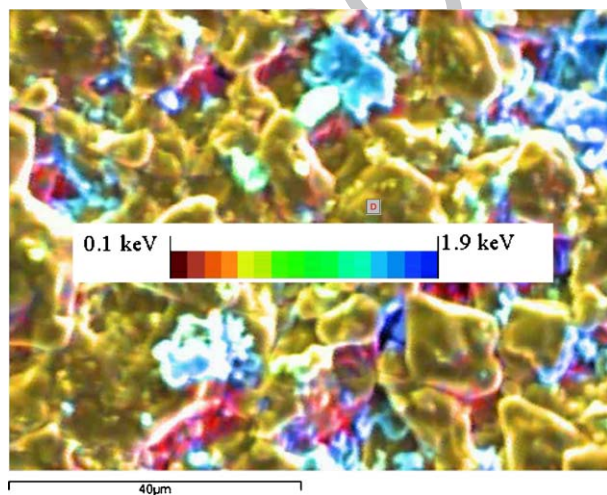


Fig. 1. Mixing of secondary electrons SEM signal and false colour characteristic X-ray maps: the colour scale is from deep red (X-ray energy 0.1 keV) to deep blue (X-ray energy 1.9 keV). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

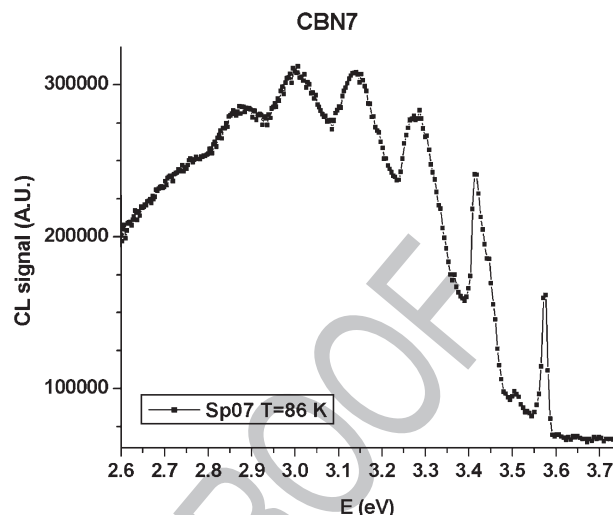


Fig. 2. High energy side of CL spectrum at grain D obtained at 86 K together with the indication of peak positions.

different grains do not show any clear structure and are dominated by a broad band centred at about 3 eV. At lower temperature peaks are clearly seen at the short wavelength side, with increasing intensities. Other small peaks in the long wavelength region, at 1.76, 1.71 and 1.63 eV, could be related to the centres called GC1 and GC2 [1], probably due to vacancies. PF1 and PF2 centres, probably related to Frenkel pairs (donor–acceptor V_N-B_i), are the first two at the left-hand side. No evidence of RC centres is appearing in this and in other spectra: since these centres should grow in the same way as BN1 as a function of irradiation dose, it is quite hard in our case to attribute the ZPL, which is found exactly at 3.293 eV (the details will be presented afterwards) and the whole vibronic structure which we are observing to a radiation induced defect strongly coupled with LO phonons.

Fig. 2 shows quite clearly the high energy side of CL spectrum with 6 equally spaced peaks: it is evident that the peak at 3.573 eV is much narrower than the other ones, with the exception of the nearby peak. This is even more evident in Fig. 3,

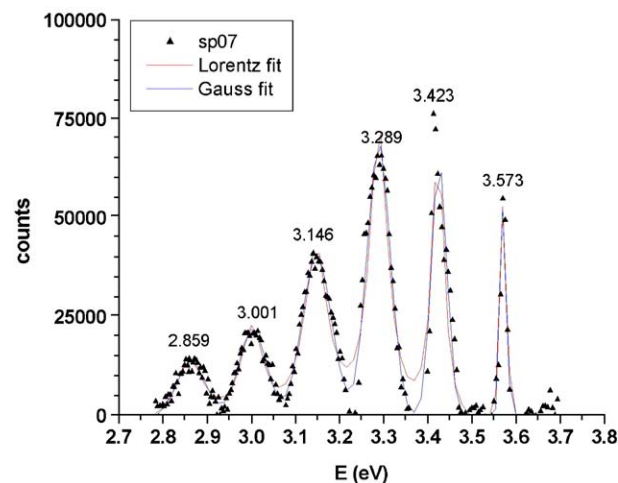


Fig. 3. Peaks observed in this figure after a “subtraction” of the fitted wide band for a better visibility.

where a “subtraction” of the fitted wide band at about 3 eV has been carried out just in order to carry out the fit. It can be observed that both the gaussian and the Lorentz fit are in good agreement with experimental data. The narrow line at 3.573 eV, fitted with a Lorentz line, displays a FWHM of about 10 meV including the contribution of the monochromator.

A full quantitative view of the results is presented in Table 1, where all the found peaks in six positions of the two samples are reported together with the mean values, the differences in energy between nearby peaks and finally the average value of the difference itself.

In our view, the best interpretation of the results is to attribute the entire spectrum, which is of course vibronic in nature, to a ZPL at 3.573 eV. In effect, some phonon replicas have been seen in c-BN by PL at low temperature and related to a BN1 centre at 3.293 eV and, moreover, by looking at Table 1, a variation of the energy difference can be observed with respect to the other peaks (even if the average distance between the first two peaks and the second two peaks is just equal to the average distance). However, the “narrow” line at 3.573 eV is much more justified as ZPL than the line at about 3.293 eV, which is a factor 2 or 3 wider. But there are other evidences: first of all, the FWHM of the whole band is about 0.83 eV: taking into account a phonon energy of 0.141 eV, this gives a Huang–Rhys factor S of 6.25. As a general rule, since the ratio between nearby peaks is given by f/S , where f is the order of the peak, we should observe a maximum of the vibronic spectrum around $f=S$, which is what we roughly see in the quoted data and in other ones obtained on different grains and on the second sample. Finally, we observe luminescence. If we attribute the first two peaks to PF1 and PF2, we are left with a Huang–Rhys factor S of about 4, while a value of 6 seems to be just the threshold above which radiative recombination is possible.

The question that remains now is: why the LO phonon energy, which has been derived from our data and which is so well defined, does not coincide exactly with LO phonon energy as derived by Raman data, which is 161.5 meV? The answer is that this energy coincide viceversa very well with LO_x phonon energy as obtained by edge CL together with a second order Raman measurement [10,11]: 140.7 meV with a SD of 2.7 meV. The interpretation now could be quite straightforward, remembering similar effects observed at former times of III–V compounds proposed for LEDs and assuming here that also in this case we are in presence of a neutral centre not substitutional but interstitial: this centre, with ZPL at 3.293 eV if due to N interstitials or with ZPL at 3.573 if due to B interstitials, as indicated above, has to be referred to the minimum of conduction band at X point in BZ of c-BN. N interstitials are not numerous in B rich c-BN and must be created by irradiation, even if they could be similar to native defects in nature. By PL it is possible to charge these centre by UV light or by 325 nm laser line [1] only if these centres are very point-like, with a wavefunction extending from X to G point and the radiative recombination is dominated by the LO phonon at the same Γ point (161.5 meV). Viceversa, by CL, these centres at 3.293 or at 3.573 eV are directly filled with much more efficiency and there is no need to create them by electron irradiation. In fact it seems

Table 1

Peaks positions (in eV) as measured in different positions or grains in two samples, together with the mean values and standard deviations, the differences (in eV) between peaks positions and the average value of phonon energy

Peak	CBN6			CBN7			Mean	SD	Diff.
	Grain A	Grain B	Grain C	Grain D	Grain E	Grain F			
1	2.720	2.722	2.721				2.721	0.001	
2	2.868	2.866	2.856	2.868	2.863		2.864	0.005	0.143
3	3.006	3.009	3.001	3.006	3.004	3.024	3.008	0.008	0.144
4	3.147	3.145	3.143	3.145	3.148	3.149	3.146	0.002	0.137
5	3.294	3.289	3.292	3.293	3.294	3.294	3.293	0.002	0.140
6	3.425	3.424	3.423	3.425	3.424	3.425	3.424	0.001	0.141
7	3.574	3.573	3.574	3.574	3.572	3.574	3.573	0.001	0.139
							Average		0.141
							SD		0.003

impossible [1] to generate these centres at 30 keV, since they can hardly created below just 200 keV. The radiative recombination, in this case, should occur with the assistance of LO_x phonons, as in the case of indirect transitions at band edge [10,11].

4. Conclusions

A rich vibronic structure with a proposed ZPL at 3.573 eV has been observed at LNT by CL on HPHT amber coloured, not intentionally doped, c-BN samples. Up to seven replicas have been observed for the first time with a very good reproducibility among different microcrystals. There is a strong evidence that ZPL is at 3.573 eV and not at 3.293 eV as previously reported [1]: as a consequence, the centre PF2 should be the first phonon replica of PF1, now identified as ZPL, and BN1 should be the second phonon replica. The phonon energy, 141 ± 3 meV, is coincident with LO phonon energy attributed to X point of BZ of c-BN and obtained by CL at indirect gap. The consequence of this coincidence is the proposed connection of the involved centre with conduction band minimum at X point. BN1 centre could be quite likely present particularly in undoped or not B rich c-BN samples, but it needs to be generated by high energy (more than 200 keV) electrons in B rich samples, in which PF1 centre (V_{N-B_i}) is more visible.

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